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Resistance of the $[Re_2(\mu\text{-dppm})_2]^{4+}$ Core (dppm = $Ph_2PCH_2PPh_2$) to Cleavage by π-Acceptor Ligands. Novel Isomers of the $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNxyl)_3]^{2+}$ Cation[1]

Wengan Wu, Phillip E. Fanwick, and Richard A. Walton*

Department of Chemistry, Purdue University, 1393 Brown Building, West Lafayette, Indiana 47907-1393

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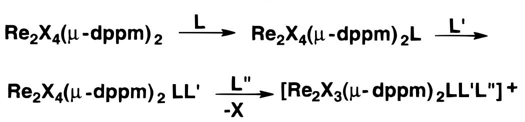
The complexes $Re_2Cl_4(\mu\text{-dppm})_2$ and $Re_2Br_4(\mu\text{-dppm})_2$ have proven to be very effective synthons in the development of the reaction chemistry of the electron-rich triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration).[2] One noteworthy aspect of this chemistry is the ability of $Re_2X_4(\mu\text{-dppm})_2$ to be complexed by π-acceptor ligands, especially CO and organic isocyanides, to afford dinuclear species in which the dppm ligand bridges play a pivotal role in stabilizing the dimetal unit,[2,3] thereby permitting the development of novel dimetal redox chemistry.[4] In the absence of the μ-dppm units, fragmentation to mononuclear species can readily occur, as happens in the case of the triply bonded complexes $Re_2X_4(PR_3)_4$,[5,6] which contain monodentate rather than bridging bidentate phosphines.

Up to three π-acceptor ligands have been incorporated into the dimetal complex in a stepwise fashion as shown in Scheme 1; in the case of compounds of types $Re_2X_4(\mu\text{-dppm})_2L$, $Re_2X_4(\mu\text{-dppm})_2LL'$, and $[Re_2X_3(\mu\text{-dppm})_2LL'L'']^+$, structural isomerism has been encountered with certain combinations of X, L, L′, and L″.[1,3,7−13] In the present report, we describe the first instances of the coordination of four π-acceptor ligands to the $(Re{\equiv}Re)^{4+}$ core to give complexes which exist in different isomeric forms. This behavior demonstrates the remarkable resistance of the $[Re_2(\mu\text{-dppm})_2]^{4+}$ moiety to cleavage and disruption of the Re−Re bonding.

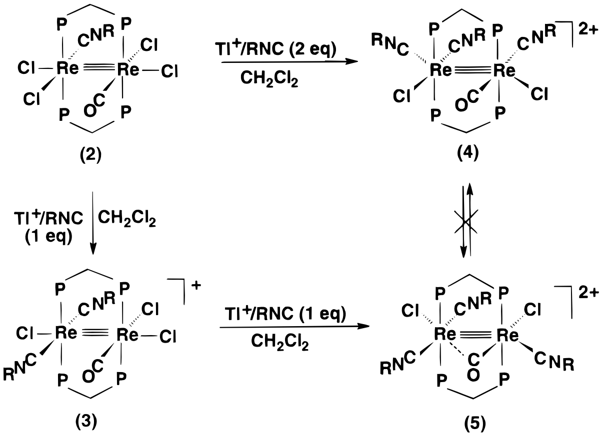
We established previously[9] that the monocarbonyl complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)$, **1**, reacts with XylNC in acetonitrile to afford the open bioctahedral complex $Re_2Cl_4(\mu\text{-dppm})_2(CO)(CNXyl)$, **2**, which in turn reacts with a further equivalent of XylNC in dichloromethane, in the presence of Tl^+, to give salts of the $[Re_2Cl_3(\mu\text{-dppm})_2(CO)(CNXyl)_2]^+$ cation, **3**. We have now found that the reactions of the neutral complex **2** and the triflate salt of **3** with equimolar mixtures of TlO_3SCF_3 and XylNC afford the salt $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3](O_3SCF_3)_2$ in two different isomeric forms (complexes **4** and **5** in Scheme 2).[14,15] We have not found any thermal conditions by which **4** and **5** can be interconverted, thereby establishing the remarkable kinetic stabilities of these two compounds.

Scheme 1. Products from the Reactions of $Re_2X_4(\mu\text{-dppm})_2$ with Carbon Monoxide and Organic Isocyanides[a]



[a] CO and the RNC ligands are represented by L, L′, and L″. In the case of the products of the types $Re_2X_4(\mu\text{-dppm})_2LL'$ and $[Re_2X_3(\mu\text{-dppm})_2LL'L'']^+$, the ligands L, L′, and L″ may or may not be the same.

Scheme 2. Routes to Isomers of the Dirhenium Cation $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNR)_3]^{2+}$ (R = 2,6-Dimethylphenyl)



The structures of crystalline **4** and **5** have been determined by X-ray crystallography.[16] The ORTEP representations of the structures of the two dirhenium cations are shown in Figures 1 and 2 and confirm that they are structural isomers. It can also be seen that the conversion of **4** and **5** (or vice versa) would require ligand dissociation to occur. The Re−Re bond lengths for **4** and **5** of 2.4728(7) and 2.4968(8) Å, respectively, are consistent with the presence of a Re−Re multiple bond. A triple

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[1] Reactions of the Dirhenium(II) Complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 14. For the previous report in this series, see: Wu, W.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1997**, *16*, 1538.

[2] (a) Price, A. C.; Walton, R. A. *Polyhedron* **1987**, *6*, 729. (b) Walton, R. A. *Polyhedron* **1989**, *8*, 1689. (c) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press; Oxford, U.K., 1993.

[3] For a recent review of this chemistry, see: Wu, W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1996**, *242*, 81.

[4] See, for example: Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1994**, *13*, 1235.

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[14] Synthesis of **4**: A quantity of **2** (100 mg, 0.0693 mmol) was mixed with 50.0 mg of TlO_3SCF_3 (0.141 mmol) and 18.5 mg of XylNC (0.141 mmol). This mixture was treated with 25 mL of dichloromethane at 25 °C, and the resulting mixture was stirred for 12 h. A solid (TlCl) was filtered off, and the brown filtrate and was reduced in the volume to ca. 2 mL. An excess of diethyl ether (20 mL) was then added to the solution to induce precipitation. The title complex **4** was harvested by filtration; yield 130 mg (97%). Anal. Calcd for $C_{81}H_{73}Cl_4F_6N_3O_7P_4Re_2S_2$ (i.e., $[Re_2Cl_2(dppm)_2(CO)(CNxyl)_3](O_3SCF_3)_2{\cdot}CH_2Cl_2$): C, 48.21; H, 3.65; N, 2.08. Found: C, 48.25; H, 3.60; N, 2.05.

[15] Synthesis of **5**: A mixture of **3** (45.0 mg, 0.027 mmol), TlO_3SCF_3 (9.5 mg, 0.027 mmol), and XylNC (3.5 mg, 0.027 mmol) in 15 mL of dichloromethane was stirred for 2 h at 25 °C. The precipitate of TlCl was filtered off, the volume of the red-brown filtrate was reduced to ca. 2 mL, and 15 mL of diethyl ether was then added to induce precipitation. The title complex **5** was collected by filtration; yield 42.3 mg (80%). Anal. Calcd for $C_{80}H_{71}Cl_2F_6N_3O_7P_4Re_2S_2$ (i.e., $[Re_2Cl_2(dppm)_2(CO)(CNxyl)_3](O_3SCF_3)_2$): C, 49.74; H, 3.70; N, 2.18. Found: C, 49.45; H, 3.71; N, 2.37.

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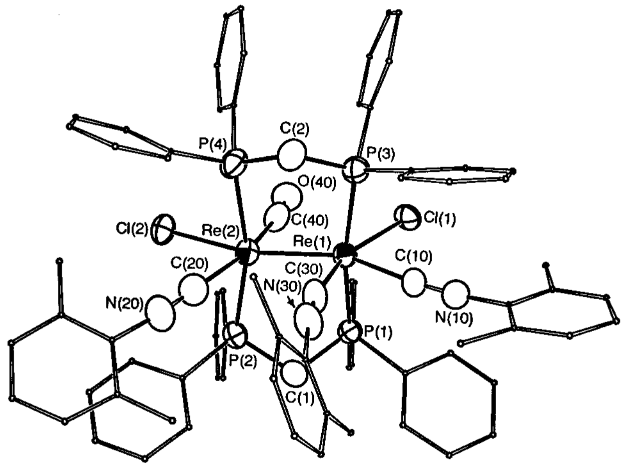

Figure 1. ORTEP representation of the structure of the $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3]^{2+}$ cation as present in **4**. The thermal ellipsoids are drawn at the 50% probability level, except for those of the phenyl group carbon atoms of the dppm ligands and the carbon atoms of the xylyl groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg): Re(1)−Re(2) 2.4728(7), Re(1)−C(30) 2.008(10), Re(1)−C(10) 2.063(9), Re(1)−Cl(1) 2.433(2), Re(1)−P(1) 2.491(2), Re(1)−P(3) 2.492(2), Re(2)−C(40) 1.961(11), Re(2)−C(20) 2.145(12), Re(2)−P(4) 2.493(3), Re(2)−Cl(2) 2.493(2), Re(2)−P(2) 2.500(3); C(30)−Re(1)−C(10) 77.6(4), C(30)−Re(1)−Cl(1) 158.6(3), C(10)−Re(1)−Cl(1) 81.0(3), C(30)−Re(1)−Re(2) 70.1(3), Cl(1)−Re(1)−Re(2) 131.28(6), C(40)−Re(2)−C(20) 165.3(4), C(40)−Re(2)−Re(1) 71.1(3), C(20)−Re(2)−Re(1) 123.6(3), C(40)−Re(2)−Cl(2) 84.6(3), C(20)−Re(2)−Cl(2) 80.7(3), N(10)−C(10)−Re(1) 174.9(8), N(20)−C(20)−Re(2) 171.1(8), N(30)−C(30)−Re(1) 165.5(8), O(40)−C(40)−Re(2) 171.8(9).

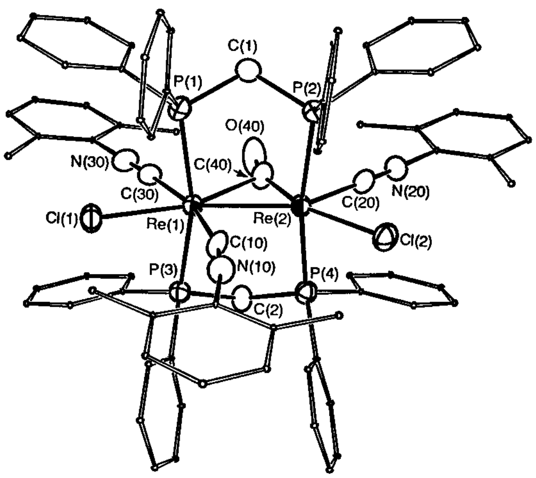

Figure 2. ORTEP representation of the structure of the $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3]^{2+}$ cation as present in **5**. The thermal ellipsoids are drawn at the 50% probability level, except for those of the phenyl group carbon atoms of the dppm ligands and the carbon atoms of the xylyl groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg): Re(1)−Re(2) 2.4968(8), Re(1)−C(10) 2.044(7), Re(1)−C(30) 2.078(7), Re(1)−C(40) 2.381(8), Re(1)−Cl(1) 2.436(2), Re(1)−P(3) 2.489(2), Re(1)−P(1) 2.491(2), Re(2)−C(40) 1.894(7), Re(2)−C(20) 2.048(8), Re(2)−Cl(2) 2.401(2), Re(2)−P(4) 2.474(2), Re(2)−P(2) 2.477(2); C(10)−Re(1)−C(30) 165.7(3), C(10)−Re(1)−C(40) 120.5(3), C(30)−Re(1)−C(40) 73.7(3), C(10)−Re(1)−Cl(1) 85.4(2), C(30)−Re(1)−Cl(1) 80.4(2), C(40)−Re(1)−Cl(1) 154.0(2), C(40)−Re(2)−C(20) 76.3(3), C(40)−Re(2)−Cl(2) 157.5(2), C(20)−Re(2)−Cl(2) 81.2(2), N(10)−C(10)−Re(1) 168.0(6), N(20)−C(20)−Re(2) 178.0(6), N(30)−C(30)−Re(1) 176.5(6), O(40)−C(40)−Re(2) 161.0(6), O(40)−C(40)−Re(1) 128.5(6).

bond, which is weakened by π-back-bonding from the metal to the RNC(π*) and CO(π*) ligand orbitals, would accord with an 18-electron count for the Re centers in these $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3]^{2+}$ cations. In the case of **5**, there is evidence for a very weak semibridging CO ligand in the solid state; the distances Re(2)−C(40) and Re(1)−C(40) are 1.894(7) and 2.381(8) Å, respectively, while the angles Re(2)−C(40)−O(40) and Re(1)−C(40)−O(40) are 161.0(6) and 128.5(6)°, respectively. The Nujol mull IR spectral properties of **4** and **5** are quite different, each showing three ν(CN) modes and a single ν(CO) mode.[17]

The $^{31}P\{^1H\}$ NMR spectrum of a solution of **4** in CD_2Cl_2 at +25 °C exhibits a sharp singlet at $\delta = -17.9$; this spectrum is unchanged down to −70 °C. These observations accord with a fluxional process by which the halves of the molecule become equivalent by a "windshield wiper" mechanism, through a symmetrical edge-sharing bioctahedral intermediate which contains μ-CO and μ-CNXyl ligands. In contrast to the fluxional behavior which occurs in solution, the solid state $^{31}P\{^1H\}$ NMR spectrum of **4** at +25 °C consists of resonances at $\delta = -16.4$, -20.5, and -35.9, which integrate to an intensity ratio of ca. 1:2:1. This spectrum is essentially unchanged upon warming the sample to +150 °C, and its complexity accords with the solid state structure as determined by X-ray crystallography (Figure 1) in which the four P atoms are magnetically inequivalent; the peak at $\delta = -20.5$ arises from the overlap of two of these resonances.

Like complex **4**, the isomeric form **5** also possesses a very simple $^{31}P\{^1H\}$ NMR spectrum which accords with fluxional behavior. A solution of **5** in $CDCl_3$ exhibits a sharp singlet at $\delta = -7.6$. The crystal structure of **5** can be considered to represent an intermediate stage in the process by which Re(μ-CO)Re and Re(μ-CNR)Re units are formed (broken) by a "windshield wiper" mechanism which renders the halves of the molecule equivalent.

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Supporting Information Available: Tables giving crystal data and data collection parameters (Tables S1 and S7), atomic positional parameters (Tables S2, S3, S8, and S9), anisotropic thermal parameters (Tables S4 and S10), bond distances (Tables S5 and S11), and bond angles (Tables S6 and S12) for **4** and **5** (25 pages). Ordering information is given on any current masthead page.

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(16) (a) Crystals of composition $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3](O_3SCF_3)_2\cdot 1.74CH_2Cl_2$, **4**, were grown from $CH_2Cl_2/i\text{-}(C_3H_7)_2O$ by slow evaporation. Crystal data for **4** (295 K): space group $P2_1/n$ (No. 14); $a = 23.582(5)$ Å, $b = 16.344(6)$ Å, $c = 23.656(6)$ Å, $\beta = 109.091(18)°$, $V = 8616(8)$ Å^3, $Z = 4$, $d_{calcd} = 1.603$ g/cm^3; Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation; 13 540 unique reflections with $5.34° < 2\theta < 48.12°$ collected and used in the refinement; all non-hydrogen atoms refined anisotropically, with hydrogen atoms included but not refined; empirical absorption correction applied (μ = 3.208 mm^{-1}); a cutoff $F_o^2 > 2\sigma(F_o^2)$ used for R factor calculations, $R(F_o) = 0.047$, $R_w(F_o^2) = 0.114$, GOF = 1.052. (b) Crystals of composition $[Re_2Cl_2(\mu\text{-dppm})_2(CO)(CNXyl)_3](O_3SCF_3)_{1.75}Cl_{0.25}\cdot 1.5C_2H_4Cl_2\cdot C_7H_8$, **5**, were grown from $1,2\text{-}C_2H_4Cl_2/C_6H_5Me$ by slow evaporation. Crystal data for **5** (295 K): space group $P2_1/c$ (No. 14); $a = 22.642(5)$ Å, $b = 13.960(5)$ Å, $c = 32.725(15)$ Å, $\beta = 109.65(3)°$, $V = 9741(11)$ Å^3, $Z = 4$, $d_{calcd} = 1.462$ g/cm^3; Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation; 19 743 unique reflections with $5.6° < 2\theta < 45.6°$ collected and used in the refinement; all non-hydrogen atoms of the cation refined anisotropically, with hydrogen atoms included but not refined; empirical absorption correction applied (μ = 2.827 mm^{-1}); a cutoff $F_o^2 > 2\sigma(F_o^2)$ used for R factor calculations, $R(F_o) = 0.045$, $R_w(F_o^2) = 0.128$, GOF = 1.107.

(17) The IR spectral properties of **4** and **5** were recorded as Nujol mulls on a Perkin-Elmer 1800 FTIR spectrometer. For **4**: ν(CN) at 2162 (ms), 2032 (ms), and 1996 (mw) cm^{-1}; ν(CO) at 1932 (vs) cm^{-1}. For **5**: ν(CN) at 2196 (m), 2166 (s), and 2056 (s) cm^{-1}; ν(CO) at 1908 (m, br) cm^{-1}.